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Description

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The present invention relates to the deposition of silicon oxide based films, and more particularly to the plasma enhanced deposition of silicon oxide based thin films from volatile organosilicon compounds.

Plasma polymerisation has been a known technique to form films on various substrates. For example, mixtures of silane with or without oxygen, nitrous oxide or ammonia have been plasma polymerised to form silicon oxide films. However, silane has a repulsive odour, can be irritating to the respiratory tract and is pyrophoric and corrosive.

Some attention turned from silane to the deposition of organosilicon films in plasmas. Sharma and Yasuda, Thin Solid Films, 110, pages 171-184 (1983) reviewed the preparation of films from several organosilicon compounds in which silicon based polymers were deposited and described the plasma polymerisation of tetramethyldisiloxane by a magnetron glow discharge with the addition of oxygen gas. The films so formed were reduced in carbon to silicon ratio with respect to the organosilicon starting material, but still retained a significant amount of carbon. However, the incorporation of oxygen in the feed mixture, despite silicon enrichment of the film, resulted in poor polymer adhesion.

US Patent No 4,557,946 describes use of plasma polymerised coatings from organosilicon compounds to form a moisture barrier on the substrate by heating the substrate and controlling the plasma power level. US Patent No 4,599,678 discloses use of an organosilicon in a glow discharge to coat thin film capacitors when these substrates are heated to a temperature in excess of 50 °C.

In general, the films formed from organosilicons have typically been formed at a relatively low deposition rate (as compared with, for example, sputtering), have tended to be soft, and often have been hazy. The requirement that the substrate be heated, as in Sacher et el. and Wertheimer et al., is also disadvantageous for some substrates.

It is an object of the invention reproducibly to deposit adherent, hard silicon oxide based, preferably thin films, preferably with preselected properties and preferably at commercially feasible deposition rates.

In one aspect of the invention, a method of depositing an adherent, hard silicon oxide based film comprises providing a gas stream with at least three components, namely a volatilised organosilicon compound, oxygen and an inert gas, establishing a glow discharge plasma derived from the gas stream, or one of its components, in a previously evacuated chamber and controllably flowing the gas stream into the plasma to a deposit a silicon oxide onto a substrate positioned in the plasma, the deposited silicon oxide being a reaction product of the gas stream and the chamber being maintained at a pressure of less than about 13.33 Pa (100 microns) during the deposition. In another aspect, the invention also includes a vacuum system according to claim 23.

The gas stream is controllably flowed into the plasma by volatilising the organosilicon exterior the chamber and admixing metered amounts with oxygen and the inert gas. An unbalanced magnetron preferably confines a portion of the plasma adjacent the substrate during the depositing which increases the ion flux and thus increases the film deposition rate.

Films of the invention can be controllably deposited on a variety of large or small substrates for applications in which a hard, protective film, or barrier, is desired. Properties of the films can be selectively modified as appropriate for particular applications.

The present invention provides a method of depositing silicon oxide based films that are hard, adherent and preferably substantially inorganic. Such films have been deposited in accordance with the invention on a variety of substrates with thicknesses between about 50 nm to 1 μ m (500 Angstroms to about 1 micron), although films thicker than 1 μ m can be obtained and are within the scope of the invention.

Choice of the substrate to be coated by the invention will vary according to the desired application. For example, various plastics such as polycarbonate resins, useful for packaging foods or beverages may be coated in accordance with the invention to prevent oxygen or moisture permeation.

Thin films in accordance with the invention may be deposited on gallium arsenide semiconductors for insulation and passivation since the substrates are not heated during practice of the invention. Glass or coated glass may be used as substrates for architectural purposes and be coated (or overcoated) in accordance with the invention. Prescription lenses of optical glass or plastic may be coated to protect against abrasion. Other applications include use of the films as orienting layers in liquid crystal displays, as laser light guides in optoelectronic devices, and in various medical applications, such as coating on activated charcoal or other substrates.

Although the process has an organosilicon compound as a starting material, the preferred films are substantially inorganic as evidenced by bonding analysis. However, films that are silicone in nature may be prepared if desired, as further described hereinafter. The typical, substantially inorganic silicon oxide based films deposited in accordance with the invention are characterised by a high degree of crosslinking

(determined by Fourier transform infrared spectroscopy, or FTIR).

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The inventive method is conducted in a previously evacuated chamber of glow discharge from a gas stream including at least three components: a volatilised organosilicon component, an oxygen component and an inert gas component. The combination of oxygen component and inert gas component with the volatilised organosilicon component has been found to greatly increase the hardness property of thin films.

As will be exemplified hereinafter, films prepared either with the organosilicon combined only with oxygen or the organosilicon combined only with an inert gas such as helium or argon has a hardness measured by the ASTM D3363-74 (standard test method for film hardness) pencil test of only 2 or 3. By contrast, films made in accordance with the invention have hardnesses by this test of about 7 to about 9 +. The numbers reported are based on a scale of 0 to 10 where 0 means the least scratch resistance, while 10 means there was no damage to the coating when abraded in accordance with ASTM D3363-74. Accordingly, thin films prepared in accordance with the invention are harder by a factor of 2 or 3 with respect to films deposited with the volatilised organosilicon component in combination with either oxygen or inert gas.

Suitable organosilicon compounds for the gas stream are liquid at about ambient temperature and when volatilised have a boiling point above about ambient temperature and include methylsilane, dimethylsilane, trimethylsilane, diethylsilane, proplysilane, phenylsilane, hexamethyldisilane, 1,1,2,2-tetramethyl disilane, bis(trimethylsilyl) methane, bis(dimethylsilyl) methane, hexamethyldisiloxane, vinyl trimethoxy silane, ethylmethoxy silane, ethylmethoxy silane, divinyltetramethyldisiloxane, divinylhexamethyltrisiloxane, and trivinylpentamethyltrisiloxane.

Among the preferred organosilicons are 1,1,3,3-tetramethyldisiloxane, hexamethyldisiloxane, vinyl-trimethylsilane, methyltrimethoxysilane, vinyltrimethoxysilane and hexamethyldisilazane. These preferred organosilicon compounds have boiling points of 71 °C, 101 °C, 55.5 °C, 102 °C, 123 °C, and 127 °C, respectively.

The volatilised organosilicon component is preferably admixed with the oxygen component and the inert gas component before being flowed into the chamber. The quantities of these gases being so admixed are controlled by flow controllers so as to adjustably control the flow rate ratio of the gas stream components.

The organosilicon compound and oxygen of the gas stream during the depositing are preferably in a flow rate ratio between about 1.2:1 to about 1:1.8, and the inert gas of the gas stream preferably is helium or argon, more preferably is helium. When the inert gas in helium or argon, then the preferred flow rate ratio of organosilicon compound, oxygen and inert gas is about 1 to 1.8:1.5 to 1.8 to 2.3.

In addition to the necessary organosilicon, oxygen and inert gas in the gas stream, minor amounts (not greater than about 1:1 with respect to the organosilicon, more preferably about 0.4 to 0.1:1 with respect to the organosilicon) of one or more additional compounds in gaseous form may be included for particular desired properties. For example, inclusion of a lower hydrocarbon such as propylene improves most properties of the deposited films (except for light transmission), and bonding analysis indicates the film to be silicon dioxide in nature. Use of methane or acetylene, however, produces films that are silicone in nature. The inclusion of a minor amount of gaseous nitrogen to the gas stream increases the deposition rate, improves the transmission and reflection optical properties on glass, and varies the index of refraction in response to varied amounts of N₂. The addition of nitrous oxide to the gas stream increases the deposition rate and improves the optical properties, but tends to decrease the film hardness. A particularly preferred gas stream composition has 20 to 40 SCCM organosilicon, 20 to 40 SCCM O₂, 40 to 60 SCCM He, 1 to 10 SCCM propylene and 5 to 20 SCCM N₂.

In practice of the invention method, a glow discharge plasma is established in the previously evacuated chamber. This plasma is derived from one or more of the gas stream components, and preferably is derived from the gas stream itself. The desired substrate is positioned in the plasma, preferably adjacent the confined plasma, and the gas stream is controllably flowed into the plasma. The substrate is preferably conveyed into and out of the plasma adjacent the confined plasma for a sufficient number of passes to obtain the desired film thickness.

The inventive method is preferably practiced at relatively high power and quite low pressure. Thus, for example, most of the films have been prepared at about 1,000 watts (40 kHz), although films have been prepared at 375 watts (13.56 MHz), and some at 300 watts, direct current. A pressure less than about 13.33 Pa (100 microns) should be maintained during the deposition, and preferably the chamber is at a pressure between about 5.7 to about 6.5 Pa (about 43 to about 49 microns) during the deposition of film.

The substrate is electrically isolated from the system (except for "electrical" contact when in the plasma) and is at a temperature of less than about 80 °C during the depositing. That is, the substrate is not deliberately heated.

The flow control is selective for desired film properties, and preferably is by a diagnostics method that includes monitoring a ratio of a hydrogen (alpha) to inert gas emission lines and an electron temperature in

the plasma. The general vacuum system in which the inventive method may be practiced and the preferred diagnostics method will now be more fully described.

To illustrate the invention, reference is made to the accompanying drawings in which:

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Figure 1 is a general schematic diagram illustrating a plasma system utilising the various aspects of the present invention;

Figure 2 schematically illustrates a side sectional view of the plasma deposition chamber and its associated equipment;

Figures 3A and 3B illustrate the use of a balanced magnetron in the system of Figure 2;

Figures 4A and 4B illustrate the use of an unbalanced magnetron in the system of Figure 2;

Figure 5 illustrates an alternative connection to a magnetron in the system of Figure 2 wherein the electric field is produced by a radio frequency generator.

Referring initially to Figure 1, a system is schematically illustrated that includes an enclosed reaction chamber 11 in which a plasma is formed and in which a substrate, such as substrate 13, is placed for depositing a thin film of material on it. The substrate 13 can be any vacuum compatible material, such as metal, glass, some plastics and other coated substrates. One or more gases are supplied to the reaction chamber by a gas supply system 15. An electric field is created by a power supply 17, and a low pressure is maintained by a pressure control system 19. An optical emission spectrometer 21 is connected through an optical fibre light transmission medium 23 to the reaction chamber in some appropriate manner to couple the visible and near visible (especially the ultraviolet range) emission of the plasma to the spectrometer. A quartz window 24 in a side wall of the reaction chamber can be used to optically couple the plasma emission with the external fibre medium 23. A general system control 25, including a computer control portion, is connected to each of the other components of the system in a manner to receive status information from them and send controlling commands to them.

The reaction chamber 11 can, in the system of Figure 1, be of an appropriate type to perform any of the plasma-enhanced chemical vapour deposition (PECVD) or plasma polymerisation processes. A more detailed explanation of certain components of the system of Figure 1 is given with respect to Figure 2, an example of the PECVD or plasma polymerisation process being given. The reaction chamber 11 is divided into a load lock compartment 27 and a process compartment 29 by an isolation gate valve 31. The pressure control system 19 includes a mechanical pump 33 connected to the load lock chamber 27 by a valve 35. The pressure control system also includes diffusion pumps 37 and 39, and an associated mechanical pump 41. The diffusion pump 37 is connected to the load lock chamber 27 through an isolation gate valve 43 and an adjustable baffle 45. Similarly, the diffusion pump 39 is connected to the process chamber 29 through an isolation gate valve 47 and an adjustable baffle 49. The baffle 49 is controlled by the system control 25, while a coating process is being carried out, in order to maintain the internal pressure at a desired value.

A substrate to be coated is first loaded into the load lock compartment 27 with the valve 31 closed. The mechanical pump 33 then reduces the pressure most of the way to the high vacuum region. The diffusion pump 37 is then operated to reduce the pressure further, to about 666.5 x 10⁻⁶ Pa (5 x 10⁻⁶ Torr). The operating pressure is typically in the neighbourhood of 6.1 Pa (46 microns) for a PECVD or plasma polymerisation process and is achieved by flowing the process gases into the reaction chamber and throttling diffusion pump 39 using baffle 49. During loading and unloading operations, the diffusion pump 39 maintains the deposition chamber 29 at the operating pressure. Once the load lock chamber 27 is reduced to base pressure, the valve 31 is opened and the substrate 13 moved into deposition chamber 29.

Provision is made for moving the substrate 13 back and forth through a region 51 where a plasma is formed. In the example system being described, this is accomplished by a plurality of rollers 53, preferably made of aluminium with substrate supporting, electrically insulated O-ring spacers. The rollers or similar material are driven by a motor source (not shown) to rotate about their axes at controllable speeds and thus move the substrate 13. A typical deposition process involves passing the substrate 13 back and forth through the plasma 51 a number of times in order that the thin film deposited on the top of the substrate 13 has a desired uniform thickness.

A magnetron is positioned within the chamber 29, formed of a magnetic structure 55 and a cathode 57. The power supply 17 has its output connected between the cathode 57 and a metallic body of the reaction chamber 29. The magnetron creates an appropriate combination of magnetic and electrical fields in the region 51 in order to create a plasma there when the proper gases are introduced into the reaction chamber 29. The substrate 13 is maintained electrically isolated and is passed directly through the plasma region 51.

The gaseous components necessary for the plasma to form in the region 51 are introduced into the deposition chamber 29 by a conduit 59. A tube (not shown) having plurality of gas supply nozzles along its length is positioned across the width of the chamber 29 (in a direction into the paper of Figure 2) at the position where the conduit 59 enters the chamber. That gas flows within the deposition chamber 29 from

the supply tube to the diffusion pump 39, as shown in dotted outline in Figure 2. It has been found preferable to introduce the gas on the side of the plasma region 51 that is closest to the pump 39. A pair of baffles 61 and 63 on either side of the magnetron also helps to confine the gas flow to the plasma region 51.

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A particular gas supply system 15 that is connected to the conduit 59 depends, of course, on how many gases are being combined and their nature. In the example of Figure 2, two separate sources 65 and 67 of gases under high pressure are utilised, fewer or additional such gas sources being necessary for other processes. also, in this particular example, a source 69 of a liquid material to be vaporised is provided. A vaporising apparatus 71 (that also controls flow) provides the desired flow of vapour into the input conduit 59, in accordance with a control signal from the system control 25. Similarly, the high pressure gases 65 and 67 are delivered through individually controlled flow meters 73 and 75, respectively. An important control of the plasma 51, and thus of the resulting film deposited on the substrate 13, is provided by the ability to adjust the proportions of each gaseous component that is flowing through the inlet tube 59 and into the deposition chamber 29. The flow meter 73 and 75 and vaporising apparatus 71 each supply the system control 25 with an electrical signal proportional to the flow rate of gas through it, and also responds to a signal from the system control 25 to adjust and control the flow rate.

The magnetron used in the plasma chamber 29 can be of a usual planar magnetron form, a representation of which is given in Figure 3A. A cross-sectional view of the magnet structure 55 is provided at a vertical plane. In plan view, the structure of Figure 3 is elongated in a direction normal to the plane of paper.

The structure of Figure 3A is termed a balanced magnetron. Its magnetic lines of force 131 all travel between one of the outer south magnetic poles and a central north pole. As is well known, electrons and ions travel in a spiral around a magnetic force line and along it, under influence of a combination of the magnetic field forces and the electric field forces formed by the cathode and the process chamber metal case. The cathode 57 is generally made of titanium or quartz, but sputtering is prevented from happening because of the higher pressure (that is, greater than the (0.13 to 0.67 Pa (1 to 5 microns) of sputtering) used in the deposition system of Figure 2.

An unbalanced magnetron that alternatively can be utilised in the system of Figure 2 is shown in Figure 4A. Outside magnets 133 and 135 are arranged with a soft iron core 137 middle. Only the south magnetic poles are positioned against a cathode 57', the north pole faces being oriented away from the cathode. The result is that a substantial proportion of the magnetic field line follow a much longer path in extending between the magnetic south and north pole regions.

Only a small proportion of the force lines extend directly between the outer south pole faces and the central iron core piece. The result is a pattern of magnetic field lines, such as lines 139 of Figure 4A, which are directed towards the substrate 13, most of them substantially perpendicular to its surface. The result is a beneficial bombardment by ions and electrons in the plasma against the surface of the substrate 13. This is known to improve some properties of the resulting deposited film, such as its hardness. Also, the deposition rate has been found to be much better with an unbalanced magnetron structure of Figure 4A rather than the balanced magnetron structure of Figure 3A.

The balanced and unbalanced magnetrons have their relative magnetic field strength distribution across the cathode indicated by diagrams of Figures 3B and 4B, respectively. As can be seen in Figure 3B, the magnetic field strength in the centre is twice the field strength of the outer poles. In the unbalanced magnetron case of Figure 4B, however, the centre field strength is very weak compared to the field strength of each of the outer magnetic poles. This difference in field strength distribution across the cathode results in the different distribution of the magnetic flux lines 139.

The magnetron structures of Figures 3A and 4A are suitable for low frequency operation of the power supply 17. An example frequency is 40 kHz. However, there can be some advantages from operating at a much higher frequency, such as in the radio frequency range of several megahertz. Such a high frequency system is schematically illustrated in Figure 5. A magnetron magnetic assembly 55" may be either of the balanced or unbalanced types described previously, the unbalanced type being preferred. The cathode 57" is in this case made of a non-conductive quartz material. A radio frequency generator 141 has its output coupled to the cathode 57" by a rod 143. An impedance matching network 145 is connected between the RF generator and the coupling rod 143 in order to minimise any reflections from impedance discontinuities at the cathode 57".

The exemplified deposition chamber 29 had a size of 305 mm x 305 mm x 610 mm (12 inches x 12 inches x 24 inches), and the vaporising apparatus 71 is believed to have a maximum flow rate of about 700 SCCM for this dimensional scale which should be adequate for most applications. However, the vaporising apparatus 71 is not limited to the exemplified dimensions since it can be readily scaled up.

Experimental

All depositions were conducted by the general procedure now described and with an "Airco Solar Products" ILS-1600 research coater. The chamber was evacuated to a base pressure of not greater than about 400×10^{-6} Pa (3 x 10^{-6} Torr). The load lock was vented to atmosphere while the chamber was maintained under high vacuum. Then the load lock was evacuated with the substrate loaded therein. Meanwhile, the vaporiser had been heated to a constant temperature of 100 °C, had vaporised organosilicon therein, but was isolated from the chamber until the gas inlet was opened. The vaporising apparatus 71 was set for the desired flow reading of organosilicon. The desired gas flows of the additional components were set on each component's flow controller, and the pressure in the chamber was adjusted to the desired value by adjusting a baffle over the diffusion pump. The load lock diffusion pump was closed and the valve isolating the load lock and the chamber was opened. After the pressure in the chamber stabilised, the power supply was turned on and adjusted to the desired value. Thus, the glow discharge plasma is established in the chamber. The pressure was again stabilised and adjusted if necessary. The desired process conditions were selected (power, current and voltage of the power supply, the pressure of the chamber, the organosilicon flow, and the vaporiser pressure). An emission spectrum from the control program was used to find the appropriate hydrogen (alpha) to inert gas ratio. The organosilicon flow into the chamber was adjusted until the desired hydrogen (alpha) to inert gas ratio was obtained. The substrate was then conveyed back and forth through the plasma region until the desired coating thickness was achieved while continuing to monitor the process conditions and making appropriate adjustments according to the diagnostic method. Once the desired film thickness was obtained, the system was shut down and the coating substrate removed.

The following abbreviations will be used:

HMDSO - hexamethyldisiloxane

TMDSO - 1,1,3,3-tetramethyldisiloxane

MTMOS - Methyltrimethoxysilane VTMS - Vinyltrimethylisilane

VTMEOS - Vinyltrimethoxysilane SCCM - Standard Cubic Centimetres per Minute

Te - Average electron temperature in electron volts

H - Hydrogen alpha emission line at 657 nm

%T - Percent transmission of light

%Rf - Percent reflection of coated side of sample

6Rg - Percent reflectance of plain glass side of sample

A haze measurement represents the percent change in haze as a result of abrading the films with an abrasive wheel (CS-10F) with a 500 g load on a Taber abrader. The hardness values (or scratch resistance) were determined by ASTM D3363-74, where 0 means the least scratch resistance and 10 means no damage to the coating when scratched.

Aspects of the inventive process are now illustrated by the following examples. All were films produced on clear glass substrates.

Example 1

Four different gas streams were used to deposit thin films on glass substrates. The power was 1,000 watts, 40 kHz. The substrate conveyor speed was 254 mm (10 inches) per minute for all four, and each substrate was passed through the plasma five times. Composition (4) was a gas stream in accordance with the invention. Table 1, below, sets out the four gas stream compositions and the scratch resistant ratings of film produced from each composition.

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Table⁻¹

Composition	Gas Stream (SCCM)	Hardness
1	20 HMDSO 20 Ar	2
2	20 HMDSO 20 He	2
3	20 HMDSO 7 O ₂	3
4	35 HMDSO 35 O ₂ 46 He	9

As can be seen from Table I, the inventive gas stream provided a film with a hardness over four times harder than gas streams including either only argon or only helium rather than both, and three times harder than a gas stream with only oxygen. The process parameters for gas stream Composition (4) of Table I were Te of 1.49 ev and H /He of 1.22. The chamber pressure varied between 5.1 and 6.1 Pa (38 and 46 microns) for the four different gas streams, and was 6.1 Pa (46 microns) for the inventive gas stream composition (4).

Example II

Five different gas streams in accordance with the invention were utilised to demonstrate use of the inventive method to select properties such as deposition rate, film dereflection and film hardness. The conveyor speed for all five was 254 mm (10 inches) per minute and the power was 1,000 watts, 40 kHz. The chamber pressure during the depositing for all five was 6.1 Pa (46 microns). Table II sets out the five different compositions and the various film and process properties.

Table-II-

5	Inventive Composition	Gas Stream (SCCM)	Hardness	Deposition Rate (nm/min)	% Rf
	5	35 HMDSO 35 O ₂ 47 He 2.1 C ₃ H ₆	7+	23.3	7.47
10	6	35 HMDSO 35 O ₂ 46 He 10 N ₂	9-	19.5	7.85
15	7	35 HMDSO 30 O₂ 46 He 5 N₂O	7	22.0	7.61
20	8	35 HMDSO 35 O ₂ 46 He 2.1 C ₃ H ₆ 6.0 N ₂	9+	22.6	7.42
25	9	36 HMDSO 30 O₂ 47 He 2.1 C₃ H₅ 9.8 N₂ O	7	20.3	6.73

As can be seen from the data of Table II, the gas stream composition (8) provided an extremely hard film, while the other four inventive gas streams gave films with good hardness at acceptable deposition rates. The film from gas stream composition (8) was formed by 37 passes, the films from gas stream compositions (5), (6) and (7) from seven passes, and that of gas stream composition (9) from five passes. Since uncoated glass has a %Rf of 7.86, the film from gas composition (9) was slightly dereflective on the coated side of the substrate. The %Rg on the plain glass side was similarly slightly reflective.

Example III

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Four different inventive gas stream compositions were utilised with different organosilicons. The pressure during deposition in all four was 46 microns, the power was 1,000 watts, 40 kHz, the conveyor speed was 254 mm (20 inches) per minute and there were five passes for each gas stream composition. The film hardnesses and two process parameters are set out in Table III.

Table-III

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Gas Stream (SCCM) Hardness Τe H/He Inventive Composition 10 39 TMDSO 1.184 1.630 45 O₂ 46 He 11 30 MTMOS 7+ 1.063 0.883 12 O₂ 90 He 12 **36 VTMS** 8 1.376 1.820 35 O₂ 46 He 30 VTMEOS 7+ 0.430 0.960 13 30 He 16 O₂

As can be seen from the data in Table III, all four different organosilicons gave films of good hardness when processed in accordance with the invention. Inventive gas stream composition (10) had a deposition rate of 38.1 nm (381 Angstroms) per minute and an oxygen transmission rate of 0.0836 cm³/645 cm²/day (0.0836 cc/100 in²/day) at a 21% oxygen atmosphere. Thus, inventive gas stream composition (10) is particularly useful for rapidly coating substrates with a film which is substantially impermeable to oxygen. Additionally, gas stream composition (12) had only a 1.01% increase in "haze" after having been subjected to 100 revolutions of the Taber abrader. This excellent "haze" value is comparable to that of clear glass, and means the coating is especially suitable for applications where abrasive resistance is needed.

30 Example IV

Two identical gas stream compositions in accordance with the invention were prepared and processed under identical conditions, except that a standard, planer magnetron was utilised for one deposition and the preferred unbalanced magnetron was used for the other. Power for both processes was 1,000 watts, 40 kHz, conveyor speed was 254 mm (20 inches) per minute with ten passes for each, pressure was 46 microns during the depositing, and the deposited films both had a hardness rating of 7. One difference between the two processes was that the preferred unbalanced magnetron had a deposition rate about 15% greater than that with the planar magnetron. The films produced by use of the unbalanced magnetron were also found to be harder when the "haze" value was determined. FTIR analysis showed a higher degree of crosslinking. Both gas stream compositions and their flow rates were as set forth in inventive composition (8) of Example II

Example V

Three similar inventive gas streams were processed with different power and/or frequency conditions. The data is set out in Table IV.

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Table-IV

5	Inventive Composition	Gas Stream (SCCM)	O ₂ Transmission Rate	Pressure (Pa)	Power	Deposition Rate (nm/min)
•	14	35 HMDSO 35 O ₂ 46 He	0.259	6.1	1000 W, 40 kHz	21.7
10	15	35 HMDSO 35 O ₂ 40 He	0.0469	6.1	375 W, 13.56 MHz	38.0
15	16	25 HMDSO 25 O ₂ 33.2 He	1.05	2.0	300 W, D.C.	62.7

The film hardnesses of gas stream compositions (14) and (15) were both 7, and that of gas stream composition (16) was 6-. Thus, it can be seen the radio frequency processing of gas stream (15) provided an excellent non-permeable property at a very good deposition rate. The deposition rate for gas stream composition (16) was outstanding, but the film had a decreased light transmission (%T of 87), increased reflectances when compared with uncoated glass. Both gas stream compositions (14) and (15) provided films having light transmission similar to uncoated glass.

Example VI

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The effect of pressure on the inventive process was studied with one composition maintained at either 13.0, 6.0 or 3.5 Pa (97, 45 or 26 microns). The deposition rates for this composition, but at three different pressures, are set forth in Table V.

Table V

Inventive Composition	Gas Stream (SCCM)	Pressure (Pa)	Deposition Rate nm/min)
17	20 HMDSO 30 O₂ 40 He 1.2 C₃H₅	13.0	9.3
17	20 HMDSO 30 O₂ 40 He 1.2 C₃H₅	6.0	14.5
17	20 HMDSO 30 O ₂ 40 He 1.2 C ₃ H ₆	3.5	17.5

As may be seen from the data of Table V, the deposition rate improves as the pressure is reduced. The hardness value for film at 3.5 Pa (26 microns) was 9+, while that of the film at 13.0 Pa (97 microns) was 9. However, a preferred pressure range is from about 5.7 to 6.5 Pa (43 to about 49 microns) because the FTIR revealed higher crosslinking.

Although the preceding examples illustrate films on clear, 3.2 mm (1/8 inch) thick glass, onto various plastics, onto metals, and onto minerals such as crystalline silicon and KBr. Thus, the method is widely applicable.

Claims

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- A method of depositing an adherent, silicon oxide based film comprising:
 providing a gas stream including a volatilised organosilicon compound, oxygen, and an inert gas;
 establishing a glow discharge plasma derived from the gas stream in a previously evacuated chamber;
 and
 - flowing the gas stream into the plasma to deposit a silicon oxide onto a substrate positioned in the plasma, the deposited silicon oxide being a reaction product of the gas stream and the chamber being maintained at a pressure of less than about 13.3 Pa (100 microns) during the depositing.
 - 2. A method according to Claim 1 in which wherein the substrate is conveyed into and out of the plasma during the depositing.
- 3. A method according to Claim 1 or Claim 2 in which the organosilicon compound is vaporised and admixed with the oxygen and the inert gas to form a gas stream outside the chamber and the gas stream is controllably flowed into the plasma inside the chamber.
 - 4. A method according to any preceding claim in which the substrate is maintained at a temperature below about 80 °C during the depositing.
 - 5. A method according to any preceding claim in which the substrate is electrically isolated from the chamber except for contact with the plasma.
- 6. A method according to any preceding claim comprising magnetically confining at least a portion of the plasma adjacent to the substrate during the depositing to increase an ion flux thereat.
 - 7. A method according to any preceding claims in which the chamber is maintained at a pressure of between about 2.7 to about 13.3 Pa (about 20 to about 100 microns) during the depositing.
- 8. A method according to any preceding claim in which the chamber is previously evacuated to about 133 x 10⁻⁶ Pa) (about 10⁻⁶ Torr) and sufficient of the gas stream is flowed into the plasma to establish a pressure in the chamber of about 3.3 to about 13.3 Pa (about 25 to about 100 microns).
- A method according to any preceding Claim in which the organosilicon compound being flowed into the
 plasma is in an adjustably controlled amount.
 - 10. A method according to any preceding claim in which the organosilicon compound and oxygen of the gas stream being flowed into the plasma are in a flow rate ratio between about 1.2:1 to about 1:1.8 and the inert gas of the gas stream being flowed into the plasma is helium or argon in an amount effective to increase the deposition rate and the hardness of the deposited silicon oxide.
 - 11. A method according to Claim 10 in which the inert gas is helium and the gas stream being flowed into the plasma comprises organosilicon compound and oxygen in a ratio in the range from about 1.2:1 to about 1:1.8 and organosilicon compound and helium in a ratio in the range from about 1:1.5 to 1:2.3.
 - 12. A method according to any preceding claim in which the organosilicon compound is 1,1,3,3-tetramethyldisiloxane, hexamethyldisiloxane, vinyltrimethylsilane, methyltrimethoxysilane, vinyltrimethoxysilane or hexamethyldisilazane.
- 50 13. A method according to any preceding claim in which the deposited silicon oxide is substantially inorganic.
 - 14. A method according to any preceding claim in which the inert gas is helium, the gas stream includes a minor amount of propylene, and the deposited silicon oxide includes carbon moieties.
 - 15. A method according to any preceding claim in which the gas stream includes a minor amount of nitrogen or nitrous oxide and the deposited silicon oxide includes nitrogen moieties.

- 16. A method according to any preceding claim in which the plasma is magnetically confined by generating within the plasma a magnetic field having a substantial magnetic flux directed against the substrate.
- 17. A method according to Claim 16 in which the step of generating a magnetic flux includes positioning within the chamber two magnetic pole pairs, a first magnetic pole of each pair being oriented to face the plasma and a second magnetic pole of each pair being oriented to face away from the plasma.
- 18. A method according to Claim 16 or Claim 17 in which the step of generating a magnetic flux includes positioning within the chamber a magnetic structure having a surface adjacent the plasma that is characterised by a magnetic flux distribution function in substantially any direction thereacross which varies from a maximum magnetic strength of one polarily separated by a lesser magnetic strength of another polarity.
- 19. A method according to any one of Claims 1 to 16 in which the plasma is confined by means of an unbalanced magnetron.
 - 20. A method according to Claim 19 in which a vacuum pump is in fluid communication with the chamber, is spaced from the magnetron, and the gas stream is flowed into the plasma upstream or a vacuum pump used to evacuate the chamber and downstream of the magnetron.
 - A method according to any preceding claim in which the substrate comprises glass, plastics, mineral or metal.
- 22. A method according to any preceding claim which includes evacuating the chamber to a pressure substantially within a range of about 5.7 to about 6.5 Pa (about 43 to about 49 microns).
 - 23. A vacuum system for use in a method of any of Claims 1 to 22 comprising: an oxygen and inert gas source and a means for delivering a controlled flow of oxygen and inert gas to a previously evacuated chamber;
 - a vaporiser for vaporising a liquid organosilane having a boiling point above ambient temperature and delivering a controlled flow of the vapour into the previously evacuated chamber;
 - electrical means for establishing a glow discharge plasma in the chamber from the vapour, oxygen and inert gas;
 - a substrate positioned within the chamber; and
 - magnetic means for generating a magnetic field within the plasma having a substantial magnetic flux directed against the substrate.
 - 24. A vacuum system according to Claim 23 further comprising at least one additional source of gas adapted to introduce the additional gas along with the vapour oxygen and inert gas into the chamber as a gas stream, and the glow discharge plasma being formed from said gas stream.
 - 25. A vacuum system according to Claim 23 or 24 in which the magnetic means includes an unbalanced magnetron positioned within the chamber.
- 26. A vacuum system according to any one of Claims 23 to 25 in which the magnetic means includes two magnetic pole pairs positioned within the chamber, a first magnetic pole of each pair being oriented to face the plasma and a second magnetic pole of each pair being oriented to face away from the plasma.
- 27. A vacuum system according to any one Claim 23 or 26 in which the magnetic means comprises a magnetic structure positioned within the chamber having a surface adjacent the plasma that is characterised by a magnetic flux distribution function in substantially any direction thereacross which varies from a maximum magnetic strength of one polarity separated by a lesser magnetic strength of another polarity.

5 Patentansprüche

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 Verfahren zum Aufbringen eines Haftfilms auf Siliziumoxydbasis, das umfaßt: Erzeugen einer Gasströmung, die eine verdampfte Organosiliziumverbindung, Sauerstoff und ein

Inertgas enthält;

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Herstellen eines aus dem Gasstrom erzeugten Glimmentladungsplasmas in einer zuvor evakuierten Kammer; und

Einleiten des Gasstroms in das Plasma zum Aufbringen eines Siliziumoxyds auf einem in dem Plasma positionierten Substrat, wobei das aufgebrachte Siliziumoxyd ein Reaktionsprodukt des Gasstroms ist und die Kammer unter einem Druck von Weniger als etwa 13,3 Pa (100 Mikron) während des Aufbringens gehalten wird.

- 2. Verfahren nach Anspruch 1, bei welchem das Substrat während des Aufbringens in das und aus dem Plasma befördert wird.
 - 3. Verfahren nach Anspruch 1 oder 2, wobei die Organosiliziumverbindung verdampft und mit dem Sauerstoff und dem Inertgas zur Bildung einer Gasströmung außerhalb der Kammer vermischt und die Gasströmung regelbar in das Plasma innerhalb der Kammer zugeführt wird.
 - 4. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Substrat w\u00e4hrend des Aufbringens auf einer Temperatur unterhalb etwa 80 °C gehalten wird.
- 5. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Substrat mit Ausnahme des Kontak-20 tes mit dem Plasma von der Kammer elektrisch isoliert ist.
 - 6. Verfahren nach einem der vorhergehenden Ansprüche, wobei mindestens ein Teil des Plasmas angrenzend an das Substrat während des Aufbringens magnetisch eingeschnürt wird, um den Ionenfluß auf das Substrat zu erhöhen.
 - 7. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Kammer während des Aufbringens unter einem Druck von zwischen etwa 2,7 bis etwa 13,3 Pa (etwa 20 bis etwa 100 Mikron) gehalten wird.
- 8. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Kammer zuvor auf etwa 133 x 10⁻⁶ Pa (etwa 10⁻⁶ Torr) evakuiert wird und eine ausreichende Gasströmung in das Plasma eingeleitet wird, um einen Druck in der Kammer von etwa 3,3 bis etwa 13,3 Pa (etwa 25 bis etwa 100 Mikron) aufrechzuerhalten.
- 9. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Organosiliziumverbindung mit einer einstellbar geregelten Menge in das Plasma eingeleitet wird.
 - 10. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Organosiliziumverbindung und Sauerstoff in der in das Plasma eingeleiteten Gasströmung in einem Strömungsmengenverhältnis von zwischen etwa 1,2:1 bis etwa 1:1,8 stehen und das Inertgas der in das Plasma eingeleiteten Gasströmung Helium oder Argon in einer Menge ist, die zur Steigerung der Aufbringrate und der Härte des aufgebrachten Siliziumoxyds wirksam ist.
- 11. Verfahren nach Anspruch 10, bei welchem das Inertgas Helium ist und die in das Plasma eingeleitete Gasströmung die Organosiliziumverbindung und Sauerstoff in einem Verhältnis in einem Bereich von etwa 1,2:1 bis etwa 1:1,8 enthält und die Organosiliziumverbindung und Helium in einem Verhältnis im Bereich von etwa 1:1,5 bis 1:2,3 stehen.
- 12. Verfahren nach einem der vorhergehenden Ansprüche, bei welchem die Organosiliziumverbindung
 1,1,3,3-Tetramethyldisiloxan, Hexamethyldisiloxan, Vinyltrimethylsilan, Methyltrimethoxsiylan, Vinyltrimethoxysilan oder Hexamethyldisilazan ist.
 - 13. Verfahren nach einem der vorhergehenden Ansprüche, wobei das aufgebrachte Siliziumoxyd im wesentlichen anorganisch ist.
 - 14. Verfahren nach einem der vorhergehenden Ansprüche, bei welchen das Inertgas Helium ist, die Gasströmung eine kleinere Menge Propylen enthält, und das aufgebrachte Siliziumoxyd Kohlenstoffanteile enthält.

- 15. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Gasströmung eine kleinere Menge Stickstoff oder Distickstoffoxyd enthält und das aufgebrachte Siliziumoxyd Stickstoffanteile enthält.
- 16. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Plasma dadurch magnetisch eingeschnürt wird, daß innerhalb des Plasmas ein Magnetfeld mit gegen das Substrat gerichtetem beträchtlichem magnetischem Fluß erzeugt wird.

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- 17. Verfahren nach Anspruch 16, wobei der Schritt des Erzeugens eines magnetischen Flusses das Positionieren zweier Magnetpolpaare in der Kammer umfaßt, wobei ein erster Magnetpol jedes Paars so orientiert ist, daß er dem Plasma zugewandt ist, und der zweite Magnetpol jedes Paars so orientiert ist, daß er von dem Plasma abgewandt ist.
- 18. Verfahren nach Anspruch 16 oder 17, wobei der Schritt des Erzeugens eines magnetischen Flusses das Positionieren einer magnetischen Struktur innerhalb der Kammer mit einer dem Plasma benachbarten Fläche umfaßt, die durch eine magnetische Flußverteilungsfunktion in im wesentlichen jeder Richtung über dieser Fläche gekennzeichnet ist, die sich von einer maximalen magnetischen Feldstärke einer Polarität, die von einer schwächeren magnetischen Feldstärke anderer Polarität getrennt ist, aus verändert.
- 20 19. Verfahren nach einem der Ansprüche 1 bis 16, wobei das Plasma mittels eines unsymmetrischen Magnetrons eingeschnürt wird.
 - 20. Verfahren nach Anspruch 19, wobei eine in Strömungsverbindung mit der Kammer stehende Vakuumpumpe mit Abstand von dem Magnetron angeordnet ist und die Gasströmung stromauf einer zur Evakuierung der Kammer verwendeten Vakuumpumpe und stromab des Magnetrons in das Plasma eingeleitet wird.
 - 21. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Substrat aus Glas, Kunststoff, einem Mineral oder Metall besteht.
 - 22. Verfahren nach einem der vorhergehenden Ansprüche, welches das Evakuieren der Kammer auf einem Druck im wesentlichen in einem Bereich von etwa 5,7 bis etwa 6,5 Pa (etwa 43 bis 49 Mikron) umfaßt.
- 23. Vakuumsystem zur Verwendung bei einem Verfahren nach einem der Ansprüche 1 bis 22, mit: einer Sauerstoff- und Inertgasquelle und einem Mittel zur Zufuhr einer geregelten Strömung von Sauerstoff und Inertgas in eine zuvor evakuierte Kammer, einem Verdampfer zum Verdampfen eines flüssigen Organosilans mit einem Siedepunkt oberhalb Normaltemperatur und zum Zuführen einer geregelten Strömung des Dampfes in die zuvor evakuierte Kammer,
- elektrischen Mitteln zum Herstellen eines Glimmentladungsplasmas in der Kammer aus dem Dampf, Sauerstoff und Inertgas, einem innerhalb der Kammer positionierten Substrat, und magnetischen Mitteln zum Erzeugen eines Magnetfelds innerhalb des Plasmas mit einem gegen das Substrat gerichteten beträchtlichen magnetischen Fluß.
 - 24. Vakuumsystem nach Anspruch 23, das außerdem mindestens eine zusätzliche Gasquelle aufweist, die zum Einleiten von zusätzlichem Gas zusammen mit dem Dampf, Sauerstoff und Inertgas in die Kammer in Form einer Gasströmung ausgebildet ist, und wobei das Glimmentladungsplasma aus dieser Gasströmung gebildet wird.
 - 25. Vakuumsystem nach Anspruch 23 oder 24, wobei die magnetischen Mittel ein in der Kammer positioniertes unsymmetrisches Magnetron aufweisen.
- 26. Vakuumsystem nach einem der Ansprüche 23 bis 25, wobei die magnetischen Mittel zwei in der Kammer positionierte Magnetpolpaare aufweisen, wobei ein erster Magnetpol jedes Paars so orientiert ist, daß er dem Plasma zugewandt ist, und der zweite Magnetpol jedes Paars so orientiert ist, daß er von dem Plasma abgewandt ist.

27. Vakuumsystem nach einem der Ansprüche 23 bis 26, wobei die magnetischen Mittel eine in der Kammer positionierte magnetische Struktur mit einer dem Plasma benachbarten Fläche haben, die durch eine magnetische Flußverteilungsfunktion in im wesentlichen jeder Richtung über die Fläche gekennzeichnet ist, die sich von einer maximalen magnetischen Feldstärke einer Polarität, die von einer schwächeren magnetischen Feldstärke anderer Polarität getrennt ist, verändert.

Revendications

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1. Procédé pour le dépôt d'une pellicule adhérente, à base d'oxyde de silicium, comprenant :

la fourniture d'un courant gazeux englobant un composé d'organosilicium volatilisé, de l'oxygène et un gaz inerte ;

l'établissement d'un plasma obtenu avec décharge luminescente, provenant du courant gazeux, dans une chambre préalablement mise sous dépression ; et

la circulation du courant gazeux pour l'introduire dans le plasma afin de déposer un oxyde de silicium sur un substrat placé dans le plasma, l'oxyde de silicium déposé étant un produit de la réaction du courant gazeux et la chambre étant maintenue, pendant le dépôt, à une pression inférieure à environ 13,3 Pa (100 μm).

- 2. Procédé selon la revendication 1, dans lequel le substrat est déplacé pour le faire pénétrer dans le plasma et pour l'en faire sortir pendant l'opération de dépôt.
 - 3. Procédé selon la revendication 1 ou la revendication 2, dans lequel le composé d'organosilicium est vaporisé et mélangé à l'oxygène, et au gaz inerte pour former un courant gazeux à l'extérieur de la chambre, et le courant gazeux est introduit en un écoulement réglable dans le plasma se trouvant à l'intérieur de la chambre.
 - 4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le substrat est maintenu à une température inférieure à environ 80 °C pendant l'opération de dépôt.
- 30 5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le substrat est électriquement isolé de la chambre, sauf pour son contact avec le plasma.
 - 6. Procédé selon l'une quelconque des revendications précédentes, comprenant le confinement magnétique d'au moins une partie du plasma au voisinage du substrat pendant l'opération de dépôt pour augmenter le flux d'ions en cet endroit.
 - 7. Procédé selon l'une quelconque des revendications précédentes, dans lequel la chambre est maintenue à une pression comprise entre environ 2,7 et 13,3 Pa (environ 20 à environ 100 μm) pendant l'opération de dépôt.
 - 8. Procédé selon l'une quelconque des revendications précédentes, dans lequel la chambre est au préalable mise sous une dépression correspondant à environ 133 x 10⁻⁶ Pa (environ 10⁻⁶ torrs) et l'on introduit par écoulement dans le plasma une quantité du courant gazeux suffisante pour établir dans la chambre une pression d'environ 3,3 à environ 13,3 Pa (environ 25 à 100 μm).
 - 9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé d'organosilicium que l'on fait pénétrer par écoulement dans le plasma circule en une quantité mesurée et que l'on peut régler.
- 10. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé d'organosilicium et l'oxygène du courant gazeux que l'on fait pénétrer par écoulement dans le plasma sont présents en un rapport de débits compris entre environ 1,2:1 et environ 1:1,8, et en ce que le gaz inerte faisant partie du courant gazeux que l'on introduit dans le plasma est de l'hélium ou de l'argon que l'on fait circuler en une quantité efficace pour augmenter la vitesse de dépôt et la dureté de l'oxyde de silicium déposé.
 - 11. Procédé selon la revendication 10, dans lequel le gaz inerte est l'hélium, et le courant gazeux que l'on fait pénétrer par écoulement dans le plasma comprend le composé d'organosilicium et de l'oxygène

présents-selon-un-rapport-compris-entre-environ-1;2:1-et-environ-1:1;8,-et-comprend-le-composé d'organosilicium et l'hélium présents selon un rapport compris entre environ 1:1,5 et 1:2,3.

12. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé d'organosilicium est le 1,1,3,3-tétraméthyldisiloxane l'hexaméthyldisiloxane le vinyltriméthylsilane, le méthyltriméthoxysilane, le vinyltriméthoxysilane ou l'hexaméthyldisilazane.

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- 13. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'oxyde de silicium déposé est essentiellement minéral.
- 14. Procédé selon l'une quelconque des revendications précédentes, dans lequel le gaz inerte est l'hélium, le courant gazeux comprend une quantité mineure de propylène, et l'oxyde de silicium déposé comprend des fragments carbonés.
- 15. Procédé selon l'une quelconque des revendications précédentes, dans lequel le courant gazeux comprend une quantité mineure d'azote ou d'oxyde nitreux, et l'oxyde de silicium déposé comprend des fragments azotés.
- 16. Procédé selon l'une quelconque des revendications précédentes, dans lequel le plasma est magnétiquement confiné par la formation, au sein du plasma, d'un champ magnétique ayant un fort flux magnétique dirigé contre le substrat.
 - 17. Procédé selon la revendication 16, dans lequel l'étape comportant la génération d'un flux magnétique inclut le positionnement, au sein de la chambre, de deux paires de pôles magnétiques, un premier pôle magnétique de chaque paire étant orienté pour faire face au plasma et un second pôle magnétique de chaque paire étant orienté dans une direction s'éloignant du plasma.
 - 18. Procédé selon la revendication 16 ou la revendication 17, dans lequel l'étape de génération d'un flux magnétique comprend le positionnement, au sein de la chambre, d'une structure magnétique ayant une surface voisine du plasma qui se caractérise par une fonction de distribution du flux magnétique dans pratiquement n'importe quelle direction transversale, qui varie depuis une valeur maximale de la force ou intensité magnétique d'une polarité, séparée par une force ou intensité magnétique inférieure d'une autre polarité.
- 19. Procédé selon l'une quelconque des revendications 1 à 16, dans lequel le plasma est confiné à l'aide d'un magnétron déséquilibré.
 - 20. Procédé selon la revendication 19, dans lequel une pompe à vide communique par du fluide avec la chambre et est espacée du magnétron et le courant gazeux est introduit dans le plasma en amont, ou bien une pompe à vide sert à mettre la chambre sous dépression et se trouve en aval du magnétron.
 - 21. Procédé selon l'une quelconque des revendications précédentes, dans lequel le substrat comprend du verre, de la matière plastique, une matière minérale ou du métal.
- 22. Procédé selon l'une quelconque des revendications précédentes, qui comprend la mise de la chambre sous une dépression correspondant à une pression se situant sensiblement entre environ 5,7 et environ 6,5 Pa (environ 43 à environ 49 μm).
- 23. Système sous dépression destiné à servir dans un procédé selon l'une quelconque des revendications
 1 à 22, comprenant une source d'oxygène et de gaz inerte et un moyen pour délivrer un débit réglé d'oxygène et de gaz inerte à une chambre préalablement mise sous dépression;
 - un vaporiseur pour vaporiser un organosilane liquide ayant un point d'ébullition supérieur à la température ambiante et pour délivrer un flux réglé de la vapeur à la chambre préalablement mise sous dépression ;
 - un moyen électrique pour établir un plasma à décharge luminescente dans la chambre à partir de la vapeur, de l'oxygène et du gaz inerte ;
 - un substrat placé au sein de la chambre ; et
 - un moyen magnétique pour engendrer au sein du plasma un champ magnétique ayant un fort flux

-magnétique-dirigé-vers-et-contre-le-substrat.-

- 24. Système sous dépression selon la revendication 23, comprenant en outre au moins une source supplémentaire de gaz adaptée à l'introduction du gaz supplémentaire avec la vapeur d'oxygène et de gaz inerte dans la chambre, sous forme d'un courant gazeux, le plasma à décharge luminescente étant formé à partir de ce courant gazeux.
- 25. Système sous dépression selon la revendication 23 ou 24, dans lequel le moyen magnétique comprend un magnétron déséquilibré placé au sein de la chambre.
- 26. Système sous dépression selon l'une quelconque des revendications 23 à 25, dans lequel le moyen magnétique comprend deux paires de pôles magnétiques placées au sein de la chambre, un premier pôle magnétique de chaque paire étant orienté de façon à faire face au plasma et un second pôle magnétique de chaque paire étant orienté dans une direction s'éloignant du plasma.
- 27. Système sous dépression selon l'une quelconque des revendications 23 à 26, dans lequel le moyen magnétique comprend une structure magnétique placée au sein de la chambre, ayant une surface voisine du plasma et qui se caractérise par une fonction de distribution du flux magnétique dans sensiblement n'importe quelle direction transversale qui varie depuis une valeur maximale de la force ou intensité magnétique d'une polarité séparée par une intensité magnétique moindre de l'autre polarité.

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